Progress Report for Innovative Research Program grant number NAGW - 4720
Title: Searching for Natural Mass Fractionation of Molybdenum Isotopes
PI: Greg Ravizza

This report covers the 12 month time period 9/1/95 to 9/1/96.

Objectives

1. To develop the mass spectrometric techniques required for the precise determination of Molybdenum (Mo) isotopic composition, using a double spiking technique to correct for instrumental mass fractionation.

2. To ascertain whether Mo isotopes can be fractionated by natural processes by applying mass spectrometric techniques (see #1) to measure the isotopic composition of Mo separated from a variety of natural materials.

I have been working towards achieving both objectives during year 1 of this project. Significant progress has been made in both areas. Work on each objective is described in turn below.

Objective 1 *Mo Mass Spectrometry.* We have successfully implemented a method for Mo isotopic analysis by negative thermal ionization mass spectrometry (NTIMS). The method is based on the work of Koppe and Heumann (1988), but we have modified the method to allow Mo isotopic analysis on a single Pt filament rather than a double filament configuration. In addition, we have also achieved enhanced sensitivity by leaking oxygen into the source of the mass spectrometer. All work to date has been performed using an electron multiplier in analog mode as the detector. This configuration allows us to achieve precision of ± 2-3 ‰ in measured isotope ratios with total analyte on the order of 100 ng Mo. While this is a significant achievement which allows high precision analyses of Mo concentrations by isotope dilution, I do not believe this precision is adequate to achieve the ultimate goal of identifying natural mass fractionation of Mo isotopes. Four separate enriched Mo isotope spikes (94Mo. 95Mo, 97Mo and 98Mo) have been purchased and prepared. These solutions will be used in our double spiking method to correct for instrumental mass fractionation. The concentration and isotopic composition of these has been determined by ICPMS. Finally, and perhaps most importantly, we have demonstrated that Mo separated from natural waters using ion exchange methods (described below) can be successfully analyzed by NTIMS without any detectable interferences from the sample matrix.

Objective 2 *Separation and analysis of Mo from natural samples.* In parallel with development of mass spectrometric methods for Mo isotopic analysis, we have established procedures for Mo separation from natural waters as well as rock and sediment samples. Separations from natural waters involves ion exchange separation using and chelating ion exchange resin based on a method resurrected

from the late sixties (Riley and Taylor 1968). For sediment analyses a procedure using anion exchange resins has been developed working from published data for Mo distribution coefficients on anion exchange resin in nitric and hydrochloric acids. Using the chelating resin procedure, we have generated Mo concentration data from an equatorial Pacific seawater profile. These data show variations in Mo concentration indicating active geochemical/biological cycling of Mo. Mo concentration data are also required in order to properly spike addition splits of these samples for high precision measurements of isotopic composition. We have not yet conducted any systematic studies of Mo concentrations in sediments or rocks, but several interesting samples are in hand and separation methods are implemented.

Year 2 Work Plan: Initially the focus of effort in year two will be on further refinement of mass spectrometric methods in order to achieve precision in all Mo isotope ratio measurements which is better than ± 0.5‰. Two problems must be surmounted to achieve this goal.

First, we must refine our existing procedure to yield larger ion beams for sample sizes on the order of 1 to 0.1 μg of Mo. The method we have developed during year 1 is very sensitive, allowing analysis of only a few ng of Mo, but maximum signal intensity does not scale linearly with the amount of total analyte. Consequently, even with relatively large sample sizes, ion beam intensities are not large enough to allow work on the faraday cup detection system. Shifting to the faraday cup is required to achieve significant improvements in the precision of Mo isotope ratio measurements We are continuing to explore different sample loading configurations and running conditions to achieve this goal.

Second, a small but persistent background Ru signal is present in Pt filament material from all vendors we have investigated thus far. Ru interferes directly on Mo isotopes with mass number 100, 98 and 96; these interferences must be eliminated to allow high precision Mo isotope ratio measurements of enough Mo isotope ratios to accurately determine the Mo isotopic composition of natural samples by the double spiking method. We are exploring alternative filament materials, as well as different sources of Pt filament to eliminate this problem.

Once these problems are solved, the separation methods implemented during year 1 will allow us to move directly to high precision spike calibrations, and analyses of natural water, sediment, rocks and material from bacterial cultures.

CERTIFICATION REGARDING
DEBARMENT, SUSPENSION, AND OTHER RESPONSIBILITY MATTERS
PRIMARY COVERED TRANSACTIONS

This certification is required by the regulations implementing Executive Order 12549, Debarment and Suspension, 34 CFR Part 85, Section 85.510, Participant's responsibilities. The regulations were published as Part VII of the May 26, 1988 Federal Register (pages 19160–19211). Copies of the regulations may be obtained by contacting the U. S. Department of Education, Grants and Contracts Service, 400 Maryland Avenue, S. W. (Room 3633 GSA Regional Office Building No. 3), Washington, D. C. 20202-4725, telephone (202) 732-2505.

(1) The prospective primary participant certifies to the best of its knowledge and belief, that it and its principals:

(a) Are not presently debarred, suspended, proposed for debarment, declared ineligible, or voluntarily excluded from covered transactions by any Federal department or agency;

(b) Have not within a three-year period preceding this proposal been convicted of or had a civil judgment rendered against them for commission of fraud or a criminal offense in connection with obtaining, attempting to obtain, or performing a public (Federal, State or local) transaction or contract under a public transaction; violation of Federal or State antitrust statutes or commission of embezzlement, theft, forgery, bribery, falsification or destruction of records, making false statements, or receiving stolen property;

(c) Are not presently indicted for or otherwise criminally or civilly charged by a governmental entity (Federal, State or local) with commission of any of the offenses enumerated in paragraph (1)(b) of this certification; and

(d) Have not within a three-year period preceding this application/proposal had one or more public transactions (Federal, State or local) terminated for cause or default.

(2) Where the prospective primary participant is unable to certify to any of the statements in this certification, such prospective participant shall attach an explanation to this proposal.

Woods Hole Oceanographic Institution — Dr. Gregory E. Ravizza

Institution — Principal Investigator

Maurice J. Tavares, Manager, Grant and Contract Services

Name and Title of Authorized Representative

Signature — 10-3-96

Date

CERTIFICATION REGARDING DRUG-FREE WORKPLACE REQUIREMENTS GRANTEES OTHER THAN INDIVIDUALS

This certification is required by the regulations implementing the Drug-Free Workplace Act of 1988, 34 CFR Part 85, Subpart F. The regulations, published in the January 31, 1989 Federal Register, require certification by grantees, prior to award, that they will maintain a drug-free workplace. The certification set out below is a material representation of fact upon which reliance will be placed when the agency determines to award the grant. False certification or violation of the certification shall be grounds for suspension of payments, suspension or termination of grants, or governmentwide suspension or debarment (see 34 CFR Part 85, Sections 85.615 and 85.620).

The grantee certifies that it will provide a drug-free workplace by:

(a) Publishing a statement notifying employees that the unlawful manufacture, distribution, dispensing, possession or use of a controlled substance is prohibited in the grantee's workplace and specifying the actions that will be taken against employees for violation of such prohibition;

(b) Establishing a drug-free awareness program to inform employees about—
   (1) The dangers of drug abuse in the workplace;
   (2) The grantee's policy of maintaining a drug-free workplace;
   (3) Any available drug counseling, rehabilitation, and employee assistance programs; and
   (4) The penalties that may be imposed upon employees for drug abuse violations occurring in the workplace;

(c) Making it a requirement that each employee to be engaged in the per-formance of the grant be given a copy of the statement required by paragraph (a);

(d) Notifying the employee in the statement required by paragraph (a) that, as a condition of employment under the grant, the employee will—
   (1) Abide by the terms of the statement; and
   (2) Notify the employer of any criminal drug statute conviction for a violation occurring in the workplace no later than five days after such conviction;

(e) Notifying the agency within ten days after receiving notice under subparagraph (d)(2) from an employee or otherwise receiving actual notice of such conviction;

(f) Taking one of the following actions, within 30 days of receiving notice under subparagraph (d)(2), with respect to any employee who is so convicted—
   (1) Taking appropriate personnel action against such an employee, up to and including termination; or
   (2) Requiring such employee to participate satisfactorily in a drug abuse assistance or rehabilitation program approved for such purposes by a Federal, State, or local health, law enforcement, or other appropriate agency;

(g) Making a good faith effort to continue to maintain a drug-free workplace through implementation of paragraphs (a), (b), (c), (d), (e) and (f).

Woods Hole Oceanographic Institution — Dr. Gregory E. Ravizza

Institution — Principal Investigator

Maurice J. Tavares, Manager, Grant and Contract Services

Name and Title of Authorized Representative

Signature — 10-3-91 Date

CERTIFICATION REGARDING LOBBYING

As required by S1352 Title 31 of the U.S. Code for persons entering into a grant or cooperative agreement over $100,000, the applicant certifies that:

(a) No Federal appropriated funds have been paid or will be paid by or on behalf of the undersigned, to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, in connection with making of any Federal grant, the entering into of any cooperative, and the extension, continuation, renewal, amendment, or modification of any Federal grant or cooperative agreement;

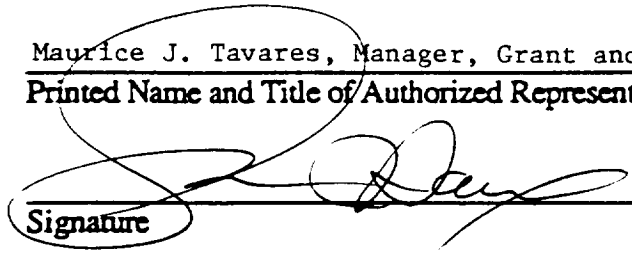
(b) If any funds other than Federal appropriated funds have been paid or will be paid to any person for influencing or attempting an officer or employee of any agency, Member of Congress, an or an employee of a Member of Congress in connection with this Federal grant or cooperative agreement, the undersigned shall complete Standard Form -LLL, "Disclosure Form to Report Lobbying," in accordance with its instructions.

(c) The undersigned shall require that the language of this certification be included in the award documents for all subawards at all tiers (including subgrants, contracts under grants and cooperative agreements, and subcontracts), and that all subrecipients shall certify and disclose accordingly.

This certification is a material representation of fact upon which reliance was placed when this transaction was made or entered into. Submission of this certification is a prerequisite for making or entering into this transaction imposed by S1352, title 31, U.S. Code. Any person who fails to file the required certification shall be subject to a civil penalty of not less that $10,000 and not more than $100,000 for each such failure.

Woods Hole Oceanographic Institution — NRA 94-OSS-16 Innovative Res. Prog.
Organization Name — AO or NRA Number and Name

Maurice J. Tavares, Manager, Grant and Contract Services
Printed Name and Title of Authorized Representative



Signature — Date: 10-3-96

Dr. Gregory E. Ravizza — Searching for Natural Mass Fractionation of Molybdenum Isotopes
Printed Principal Investigator Name — Proposal Title